

Eliminating the Detrimental Effects in Solid-State Batteries

A bidirectionally compatible buffering-layer enables a highly stable and conductive interface for sulfide-based all-solid-state lithium batteries.

All-solid-state lithium batteries (ASSLB) are regarded as one of the next-generation energy storage technologies to compete or even to surpass the state-of-the-art liquid-based lithium-ion batteries. By replacing organic liquid electrolytes with non-flammable solid electrolytes (SE), ASSLB are expected to address safety concerns associated with flammable organic electrolytes, and to achieve applications over a wide temperature range. Among SE of various types, sulfide is viewed as one of the most promising SE candidates for the commercialization of high-performance ASSLB, but the narrow electrochemical stability window of sulfide SE challenges the interface stability especially at the high-voltage cathode side, thus producing much increased interfacial resistance, poor rate performance and rapid capacity fading. Moreover, the structural mismatch and electrochemical potential discrepancy between oxide cathodes and sulfide SE render high interfacial impedances for Li-ion transport. These phenomena limit the realization of sulfide SE in high-voltage battery systems for increased energy densities.

Guanglei Cui (Chinese Academy of Sciences, China) and his coworkers recently found that $\text{Li}_x\text{Zr}_2(\text{PO}_4)_3$ (LZPO) served as a proof of concept for a bidirectionally compatible buffering-layer design scheme (Fig. 1) to overcome the interfacial challenges of sulfide-based high-voltage ASSLB (HVASSLB). Employing X-ray absorption spectra (XAS) at **TLS 16A1**,¹ the mechanism of improvement of the LZPO buffering layer on interfacial stability and Li-ion transport dynamics was studied. As shown in Fig. 2, the S K-edge and P K-edge on the composite cathode side were characterized using the fluorescence-yield mode to investigate the interface stability between $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) and LiCoO_2 (LCO) with and without the LZPO buffering layer. An effective chemical stability between LZPO-LCO and LPSCI was observed. In contrast, LPSCI is thermodynamically unstable with LCO but undergoes spontaneous decomposition in contact with LCO. It was concluded that the LZPO buffering layer can remarkably enhance the stability of the LCO/LPSCI interface and the Li-ion transport dynamics even cycled at voltage 4.5 V, which

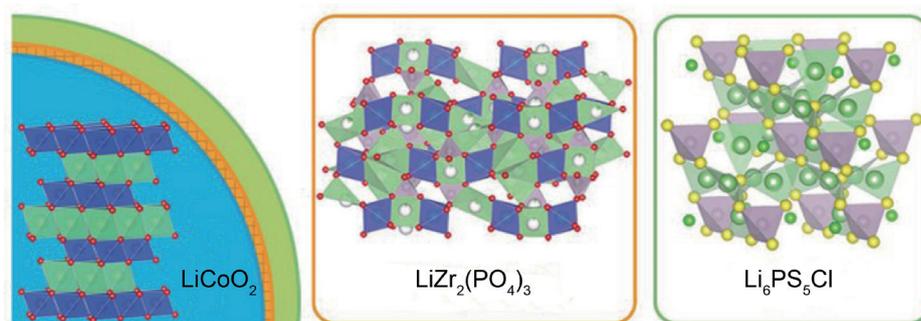


Fig. 1: Schematic illustration of the design of a bidirectionally compatible buffering layer. [Reproduced from Ref. 1]

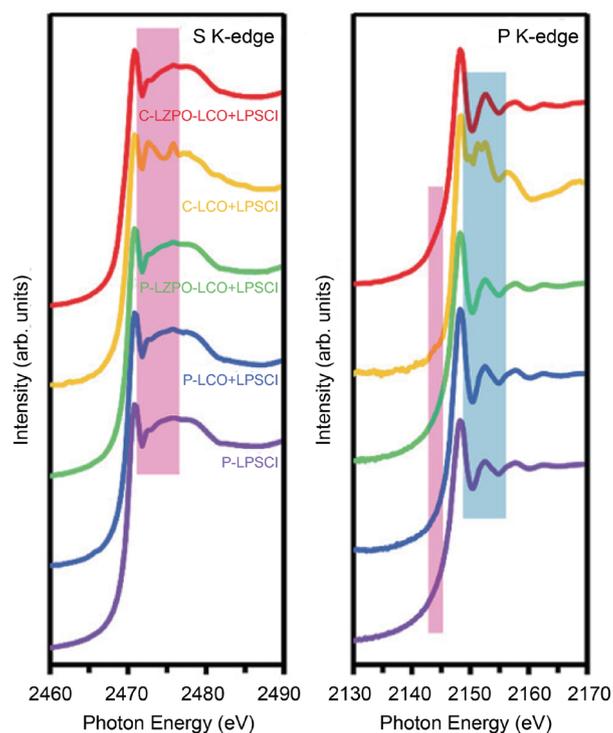


Fig. 2: XAS at S K-edge and P K-edge for pristine LPSCI (P-LPSCI), pristine LCO/LPSCI composite cathode (P-LCO/LPSCI), pristine LZPO-LCO/LPSCI composite cathode (P-LZPO-LCO/LPSCI), LCO/LPSCI composite cathode after 100 cycles (C-LCO/LPSCI), and LZPO-LCO/LPSCI composite cathode after 100 cycles (C-LZPO-LCO/LPSCI). [Reproduced from Ref. 1]

confirms the feasibility and great prospects of NASICON-type LZPO coatings for sulfide-based HVASSLB.

In summary, NASICON-type LZPO with high oxidation limits and reasonable ionic conductivity was demonstrated as a proof of concept for a bidirectionally compatible buffering-layer design scheme to overcome the interfacial challenges of sulfide-based HVASSLB. 4.5-V LZPO-LCO/LPSCI/In-Li HVASSLBs could thereby exhibit an initial discharge capacity up to 143.3 mA h g⁻¹ at 0.2 C, and excellent long-cycle performance (95.53% capacity retention after 100 cycles). This work sheds light on the great prospects of sulfide-based HVASSLB with high-rate characteristics, and constitutes a crucial step toward the rational design of the interface and interphase chemistry for high-performance sulfide-based HVASSLB. (Reported by Yan-Gu Lin)

This report features the work of Guanglei Cui and his collaborators published in Adv. Energy Mater. 11, 2100881 (2021).

TLS 16A1 Tender X-ray Absorption, Diffraction

- XANES, EXAFS
- Materials Science, Chemistry, Condensed-matter Physics, Environmental and Earth Science

Reference

1. L. Wang, X. Sun, J. Ma, B. Chen, C. Li, J. Li, L. Chang, X. Yu, T.-S. Chan, Z. Hu, M. Noked, G. Cui, *Adv. Energy Mater.* **11**, 2100881 (2021).

Catching Hidden Structural Evolution in Near-Infrared Phosphors

The random distribution of Ga³⁺ and Sc³⁺ ions at the Ga2 site of Ga₂O₃ greatly affects the photoluminescent properties.

Recently, phosphor-converted IR light-emitting diodes (pc-IR LEDs) have evolved into smart devices with the advantages of large output power, high efficiency and small size. IR phosphor materials are crucial components of these devices, affecting the overall performance of the resulting spectrum. Cr³⁺, as a unique and ideal near-IR emitter that can produce either sharp-line or broadband spectra, has become a promising candidate for producing IR light. Although substantial progress has been achieved in this popular topic, most studies have focused on a single compound or on changing activators without systematically tuning the crystal structure and the luminescent wavelength. Consequently, understanding the control mechanism is considered an important issue in tuning luminescent properties. Some local structural distortions or phase transitions might result in unexpected photoluminescent properties. Moreover, a subtle change in the local structure might tune photoluminescence between sharp-line or broadband emissions. This phenomenon has been seldom discussed in previous studies. The overall tuning mechanism remains vague.

Ru-Shi Liu (National Taiwan University) and his coworkers recently conducted a complete study on the unexpected structure evolution behavior in Cr³⁺-doped phosphors. Ga_{1.994-x}Sc_xO₃:0.006Cr³⁺ (Ga_{2-x}Sc_xO₃:Cr³⁺) phosphors in a series were synthesized; their unique structural

and photoluminescent properties were characterized, demonstrating their high potential in IR-LED applications. Employing X-ray diffraction (XRD) measurements at beamline **TLS 01C2**,¹ the unique partial substitution (~87%) of Sc³⁺ in the octahedral site was demonstrated *via* Rietveld refinement. The synchrotron XRD patterns of Ga_{2-x}Sc_xO₃:Cr³⁺ phosphors with varied Sc³⁺ concentration are shown in **Fig. 1(a)**. The pure phase was obtained at $x = 0-0.8$; Sc₂O₃ impurities existed at $x = 1$ and 1.2. The diffraction signals shifted toward lower angle on incorporation of Sc³⁺ ions because of the ionic size of Sc³⁺ (0.745 Å; CN = 6) larger than that of Ga³⁺ (0.47 Å; CN = 6) (CN denotes coordination number). Unexpectedly, the diffraction peaks did not shift linearly for $x > 0.8$. This finding might indicate the failure of the Sc³⁺ doping when $x > 0.8$. To investigate this unique behavior in-depth, Rietveld refinements of Ga_{2-x}Sc_xO₃:Cr³⁺ were conducted and analyzed. The lattice parameters, namely, a , b , c , and V , linearly increased for $x = 0-0.8$, as shown in **Fig. 1(b)**. The speed of ascent decreased from $x = 0.8-1.0$ and even stopped increasing from $x = 1.0-1.2$. To understand this property, the crystal structure and local coordinated environment of Ga₂O₃ were also carefully examined. Ga₂O₃ possesses a monoclinic structure with space group C2/m. Two distinct Ga³⁺ sites, namely, Ga1 and Ga2, were found in the Ga₂O₃ structure. Ga2 is coordinated with six O²⁻ forming an octahedron; Ga1 is coordinated by four O²⁻ forming a tetrahedron. When introducing Sc³⁺ into